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REPORT

of

COMMITTEE ON THESIS

THE undersigned, acting as a committee of the Graduate School. have read the accompanying thesis submitted by Mildred R. Ziegler for the degree of Master of Arts. They approve it as a thesis meeting the requirements of the Graduate School of the University of Minnesota, and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of ~~Arts.~~ Science

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A Contribution to the Knowledge of the Reimer Tiemann Reaction. The Role of the Potassium Hydroxide.

A Thesis

Submitted to the Faculty of the Graduate School

of the University of Minnesota

by

Mildred H. Ziegler

In partial fulfillment of the requirements for

the degree of

Master of ~~Arts~~ Science .

1915

A Contribution to the Knowledge of the Reimer Tiemann Reaction. The Role of the Potassium Hydroxide.

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The Reimer-Tiemann reaction is a method for the preparation of oxyaldehydes or oxyacids from phenols having the ortho or para positions open. The general method of preparation of an aldehyde according to this reaction consists in dissolving the required amount of phenol in a strong solution of potassium hydroxide. The mixture is carefully heated to 60° or 70° in a flask fitted with a reflux condenser, and chloroform is slowly added thru the reflux. If it is added too rapidly the boiling chloroform causes the liquid to be forced out of the condenser. After the reaction mixture has been heated to boiling the unchanged chloroform is distilled off, the alkaline solution acidified and distilled with steam. The phenol and aldehyde pass over with the steam. The mixture is extract-

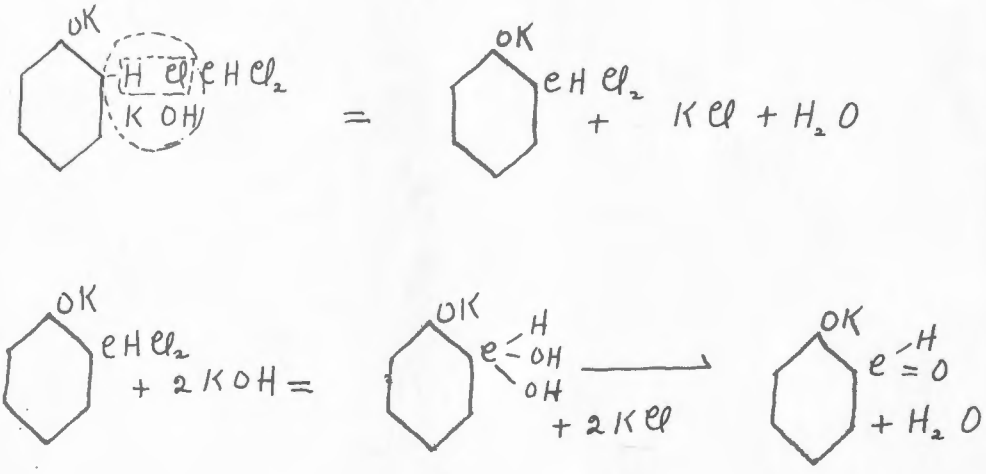
ed with ether and the ether treated with a saturated solution of sodium bisulphite which adds to the aldehyde forming the sodium bisulphite compound of the aldehyde. The ether is then separated and the water solution treated with sodium carbonate which frees the aldehyde. It is extracted with ether and distilled. The yield is never very good.

It is useful because it furnishes a method like the Kolbe synthesis of adding one more carbon atom to the benzene ring. In the original paper published by Reimer and Tiemann in the year 1876* a comparison was made between the two reactions. It was suggested that the chloroform and potassium hydroxide might react to produce formic acid which brings about an interposition as the carbon dioxide does in the Kolbe synthesis.

It has long been believed that the chloroform in the presence of phenol and potassium hydroxide adds to the ring splitting out hydrochloric acid which is taken up by the potassium hydroxide.

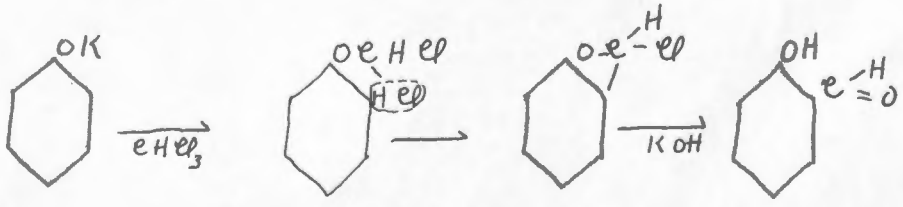
The potassium hydroxide then acts on this addition product to form aldehydes.

* B 9, 824 (1876).



This seems to have been the general conception, but as little work has been done on the reaction it has not been questioned a great deal.

Mr. Goldstein* thought that the reaction might occur at the potassium of the phenolate like ether and ester formations, but his evidence did not seem to favor this formation.

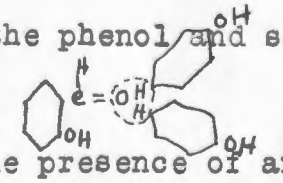


* Senior thesis unpublished.

We have attempted to show how the potassium hydroxide acts. Probably its function is to abstract the hydrochloric acid split out when the chloroform reacts at the ring. We hoped by showing the influence of the potassium hydroxide to throw some light on the mechanism of the reaction.

The reactions of the three constituents present are exceedingly complex, too complex to study by velocity reactions.* There are at least four distinct reactions possible in the solution.

The potassium phenolate reacts to form a red dye of the rosolic acid series. According to the work of Dale and Schlormmer it is formed by the dehydrating effect of the alkali on the phenol and salicyaldehyde as shown by this formula.



It may form in the presence of anhydrous chloroform ortho formic ester(triphenoxy methane) which is not affected by alkalies, but is split by acids. No red dye is produced at the same time except with hot vapor of chloroform.

$$3\ C_6H_5OK \xrightarrow{CHCl_3} (C_6H_5O)_3CH + 3KCl$$

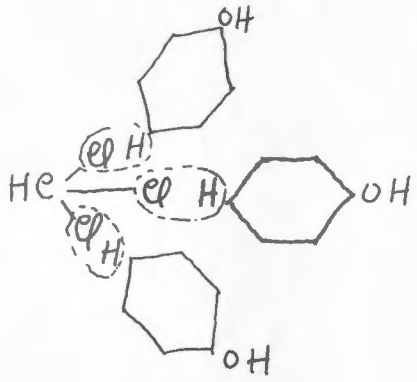
* Cf. p. 6.- Saunders on K O H C H Cl .

P.oxy benzaldehyde and salicyaldehyde are also formed, the former only in potash, never in soda solution. These products are obtained at a much lower temperature than the dye.

The formation of red dye in the reaction can also be explained by analogy with the research of F. Heiber* on the action of benzotrichloride, trichlormethylmethane, and alkali phenolate solutions, which shows that several reactions occur at once giving dyes, orthoformic esters, and phenol aldehydes. He proved that during the action of these three chemicals the same series of reactions occurred as in the Reimer Tiemann reaction. This is the last published article from Tiemann's laboratory which refers specifically to the Reimer Tiemann reaction.

Then, by analogy with this work, in the Reimer Tiemann reaction, the $C H Cl_3$ would react directly with the phenolate to form the red dye, as indicated by the following diagram:

* B 24, 3677 (1891)



Beside the above side reaction, the potassium hydroxide is also acting on the C H Cl_3 independently. It is well known that potassium formate results from this reaction, but it is not so generally recognized that carbon monoxide is also formed. Saunders* worked on the action of potassium hydroxide and chloroform in alcohol, by determining the velocity of the reaction. His constants were varying but apparently showed that the reaction is of the third order. He states that the reaction takes place in stages in each of which two molecules react together. He attributed his varying results to the fact that the water formed may dis-

* J. Ph. Ch. 4,660 (1900)

turb the reaction.

Since there are so many reactions occurring at the same time, it seemed best not to try to measure the velocity of the reaction in the ordinary manner, as this would not throw any light on our problem, but to determine the relative velocities under changing concentrations of K O H and K O $C_6 H_5$.

To get at this, we have assumed that the halogen removed in the reaction is chiefly that from C H Cl_3 forming aldehyde. Other sources for halogen are the reactions forming the red dye and the actions of the chloroform with phenolate and potash, of which only the halogen formed by red dye making cannot be determined separately and subtracted to correct the total halogen formed.

The method employed was very simple. The phenol and potassium hydroxide was heated with the free flame until the potassium phenolate had dissolved. The flask was fitted with a reflux condenser thru which the chloroform was added as soon as the phenolate had dissolved. The time at which it came in contact with the solution

was noted to seconds; the mixture heated ten minutes; at the end of that time the heating was stopped; cold water was poured thru the condenser and the contents of the flask were immediately emptied into 200 c.c. of cold water acid with nitric. If the mixture was not acid more nitric was added. This happened in but two determinations of 90% and 100% of Curve I. The chloroform was separated, washed, and the washing added to the main volume which was made up to 500 c.c. in a calibrated flask. 50 c.c. portions were removed with a calibrated pipette and titrated for chlorine with silver nitrate and potassium sulphocyanate. The results obtained were plotted, the grams of chlorine on the ordinate and the per cent of phenol on the abscissa. This gave the one large curve in which the chlorine removed represents the aldehyde formation.

The greatest error in the above method seemed to be the difference in temperature caused by the varying

vapor pressure of the potassium hydroxide solution. It resulted that this did not make so much difference when the phenol, potassium hydroxide and chloroform were present in the determination of "total halogen" or"Curve I."

The same technique was applied to obtain correction curves, using potash only and potassium phenolate only, when it became evident that in comparison to the main reaction in which all three are concerned, the amounts of halogen removed are small. This was a very welcome result, giving but small corrections to be applied. It was found, however, that the K O H determinations were very sensitive to temperature changes, for when carried on in the former manner, the determinations did not check. It is possible that with changing temperature the formation of some other product disturbed the results, as the formation of H_2O disturbed the results of Saunders. The method was remedied by keeping the reaction mixture at a temperature of 55° in a thermostat which was constant to one-tenth of a degree. 65°, 62°, and

60° baths were tried, but it was found that the mixture boiled at that temperature. It was desired to prevent boiling in order to eliminate the great change of vapor pressure in the boiling mixture. It is an objectionable feature that the determinations of the large curve were heated ten minutes and those of the correction curves twenty minutes. Perhaps both should have been heated the same time, but it was not practical to heat the correction points ten minutes, as the amount of chlorine removed in that time was so small while a very large amount of chlorine would have been obtained if the phenol, potassium hydroxide and chloroform had been heated twenty minutes. It was decided to run the correction curves twenty minutes and take one-half of the results for the correction. This causes a slight error as the velocity of the reaction probably varies during that time, but as it has been pointed out the corrections are small.

Since the reaction is occurring between two liquids, careful attention was paid to the question of

mixing. This was accomplished thoroughly by the vaporization of the chloroform in the case of the "total halogen curve" and the phenolate curve (Correction Curve I). In the case of the chloroform and potassium hydroxide curve the reaction mixture was kept below the temperature of boiling chloroform so that it was necessary to stir those determinations by air. Therefore 50 c.c. of chloroform were used in order to have some left at the end of the reaction as the air stirring vaporized a great deal.

The results obtained were in the form of six curves, one total halogen curve uncorrected, two correction curves, one total halogen curve corrected, and two total halogen curves recalculated from the original to show the effect of varying phenolate with constant potassium hydroxide and the reverse.

The large curve in which the hydroxyl and phenoxyl groups are varied while the potassium is held constant gave a curve in which the maximum is attained at 17%, rising rapidly from 0% and then gradually

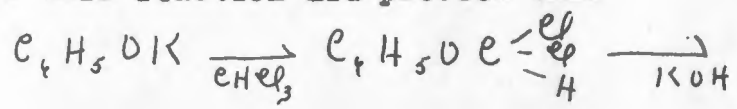
falling off along the line of concentration of the potassium hydroxide. It seems that it is due to the fact that the conditions for the Reimer Tiemann reaction are gradually approached and then that the potassium hydroxide which is the leading factor regulates the course of the reaction.

In the correction curve for the action of the phenolate it is shown that hydrolysis has a great effect. If the concentration only was concerned, a straight line would probably result, but with increasing concentration the amount of halogen removed increases, showing that there is a reaction like that of any mixture of K OH and K O C H the K O H resulting from the hydrolysis.

For the correction curve for potassium hydroxide and chloroform, the one obtained by using the thermostat was of course applied, as the results were more accurate as before mentioned. The shape of this curve is probably due to the hydroxyl ions as dissociation is greatest at the lower concentration, or possibly several reactions occur which influence its shape.

These results seem to indicate that potassium

hydroxide determines the reaction; that the formation of aldehyde would not occur without the presence of K O H. The results also seem to show that it causes the chloroform to react with the ortho hydrogen instead of the potassium of the phenolate. The action of potassium phenolate and chloroform, if the action goes to completion, forms triphenoxy methane which is not affected by alkalies. If alkalies have no effect on this then, since the potassium hydroxide has most influence as shown by the curves, the reaction would occur at the ortho hydrogen in preference to the — OK. Hence the aldehyde does not result from the reaction that yields the triphenoxymethane. However, there is the possibility of the action not going to completion and phenoxy dichlormethane might be formed which would be capable of going to the aldehyde. But this hardly seems possible as pyridine and calcium carbonate substituted for potassium hydroxide apparently did not produce the same effect as the potassium hydroxide. If this reaction did proceed thus



aldehyde

you would expect that the amount of chlorine removed would increase with the phenolate, which is not true according to the curve. The curve shows that the amount of chlorine decreases with an increase in phenolate.

Another point against this formation of phenoxy dichlormethane is that Mr. Goldstein found that dry potassium phenolate and dry chloroform vapor did not react to form chlorides, as no test for chlorides could be obtained at 85°. At 100° the red dye was produced showing a reaction and giving a test for chlorides. "The absence of chlorine containing bodies and the large quantity of red dye tend to indicate that the ring is attacked in the ortho position." Some determinations made with carbon tetrachloride and potassium hydroxide with and without phenol, and those made with benzotrichloride and potassium hydroxide with and without phenol, showed that these chlorides are much less reactive than the chloroform. It is known that carbon tetrachloride reacts with phenolate and alkali in the same manner as chloroform, forming an acid in-

stead of an aldehyde. Since it cannot split to form — C=O or — $C\overset{Cl}{\underset{Cl}{<}}$, by loss of H Cl it seems that it reacts first with the ortho hydrogen and then that the other chlorines are cared for by the potassium hydroxide, and that the chloroform probably reacts in an analogous manner.

It is yet to be determined why the ortho hydrogen cannot react in this way without the potassium hydroxide, for as thus far determined it has been shown that phenolate and chloroform do not form aldehyde alone or in the presence of bases like calcium carbonate and pyridine. Probably the same explanation would apply here as in the similar reactions of Freidel and Craft and Gatterman's aldehyde synthesis.

Summary:—

Our results seem to bear out the following conclusions:

The common idea is correct that the chloroform reacts with the hydrogen ortho to the hydroxyl group.

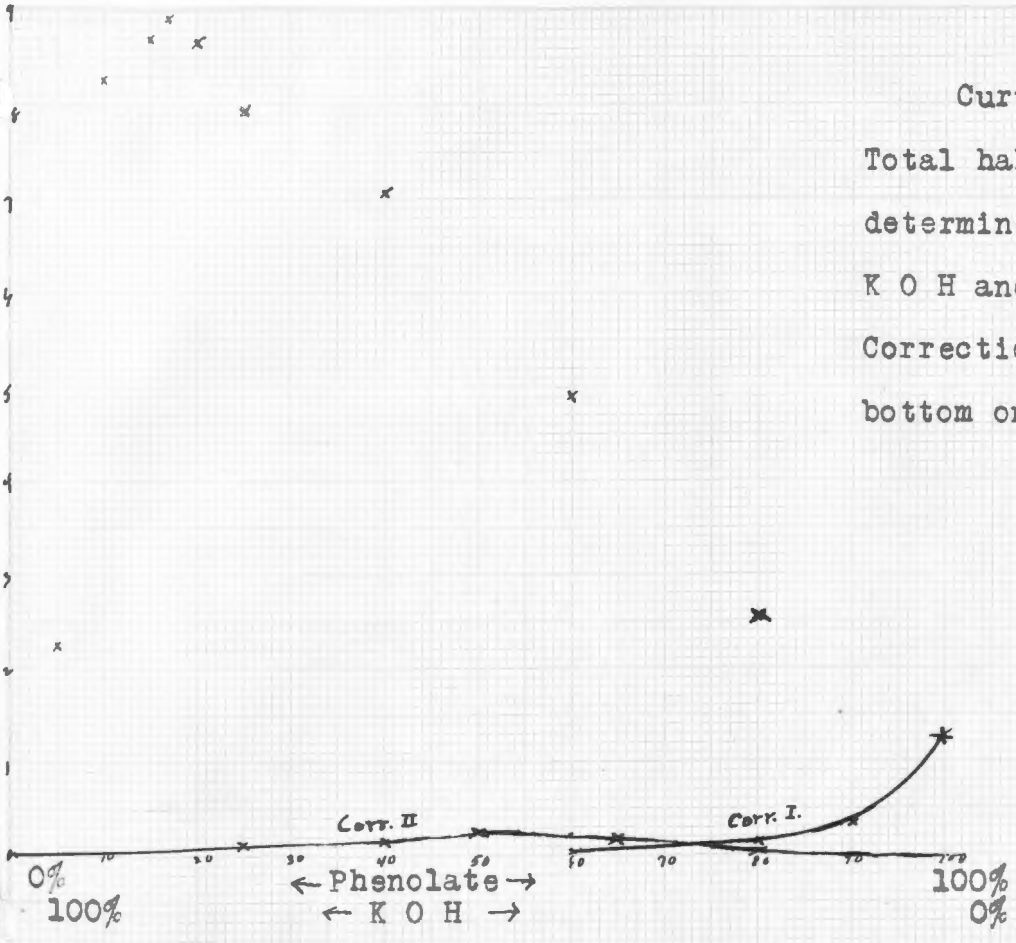
No aldehyde is formed without the presence of potassium hydroxide.

The velocity of the reaction varies directly as the concentration of the potassium hydroxide.

After a certain amount of potassium phenolate is present the velocity of the reaction is not affected by a change in concentration.

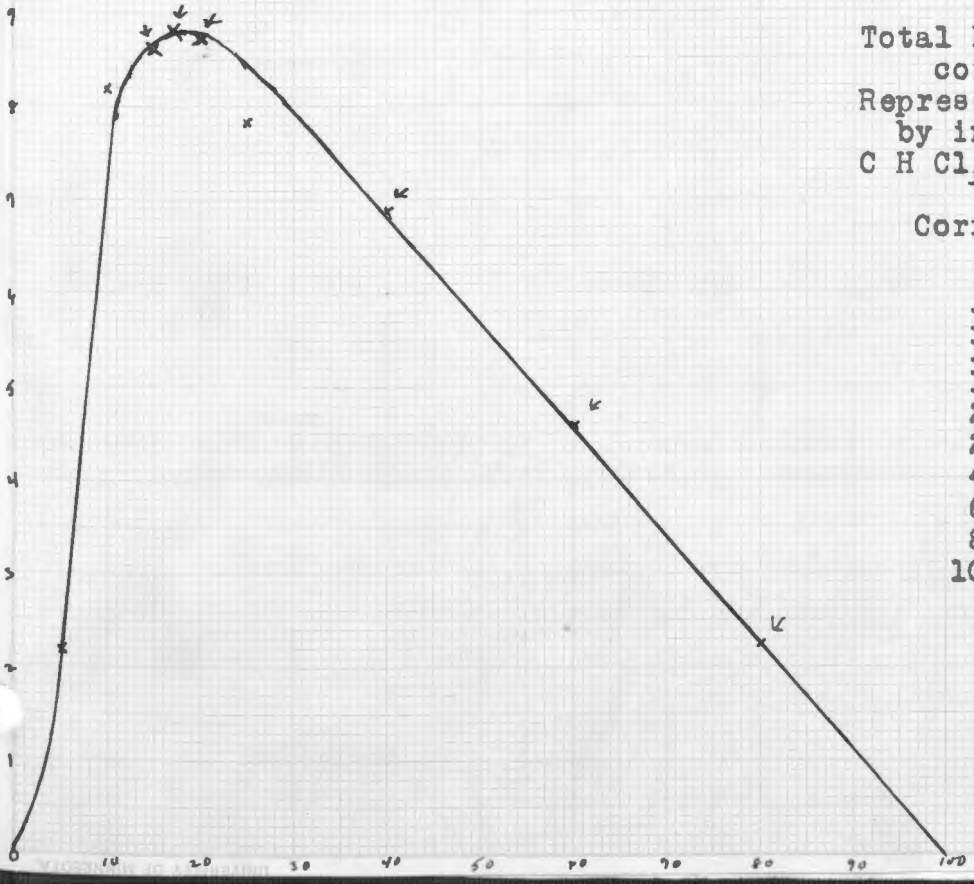
This is a strictly abstraction reaction.

This differentiates it from the Kolbe synthesis.



Curve I.

Total halogen as determined, varying K O H and C_6H_5OK. Correction curves at bottom on same scale.



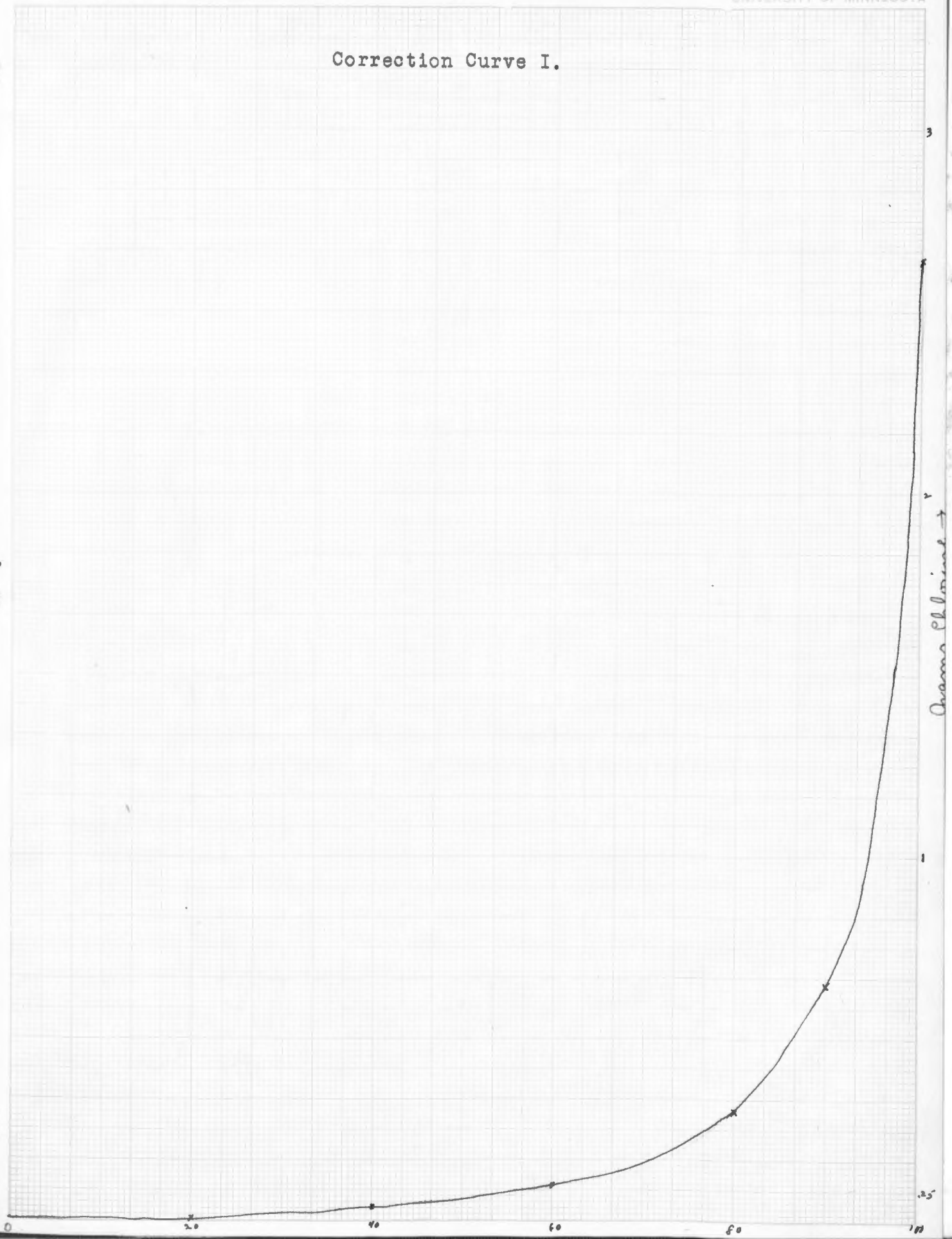
Curve II

Total halogen curve corrected.
Represents halogen removed by interaction of
C H Cl_3, K O H, & C_6H_5OK

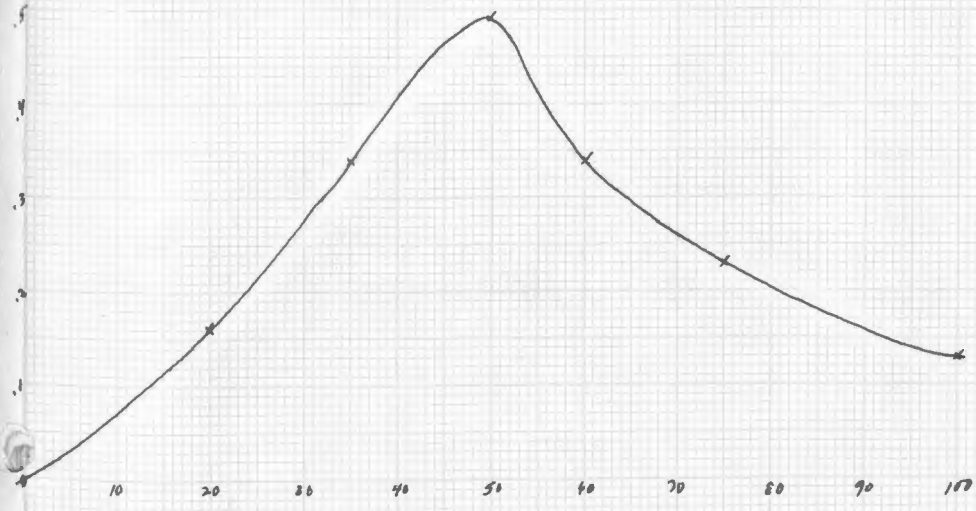
Corrected values

0 - 0
5 - 3.28
10 - 8.20
15 - 8.62
17 - 8.82
20 - 8.57
25 - 7.84
40 - 6.92
60 - 4.61
80 - 3.27
100 - 0

Correction Curve I.



Correction Curve II.

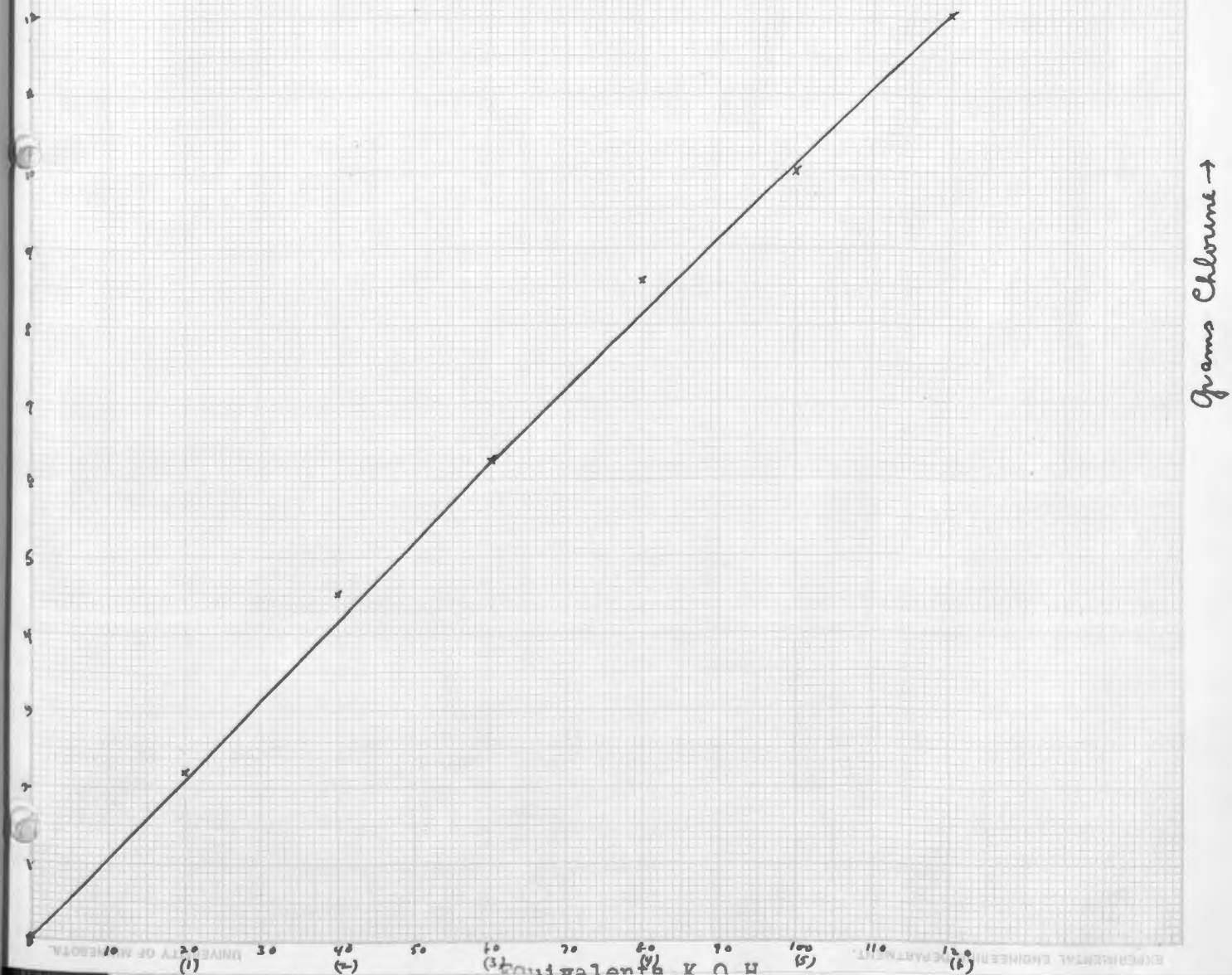


← Grams Chlorine

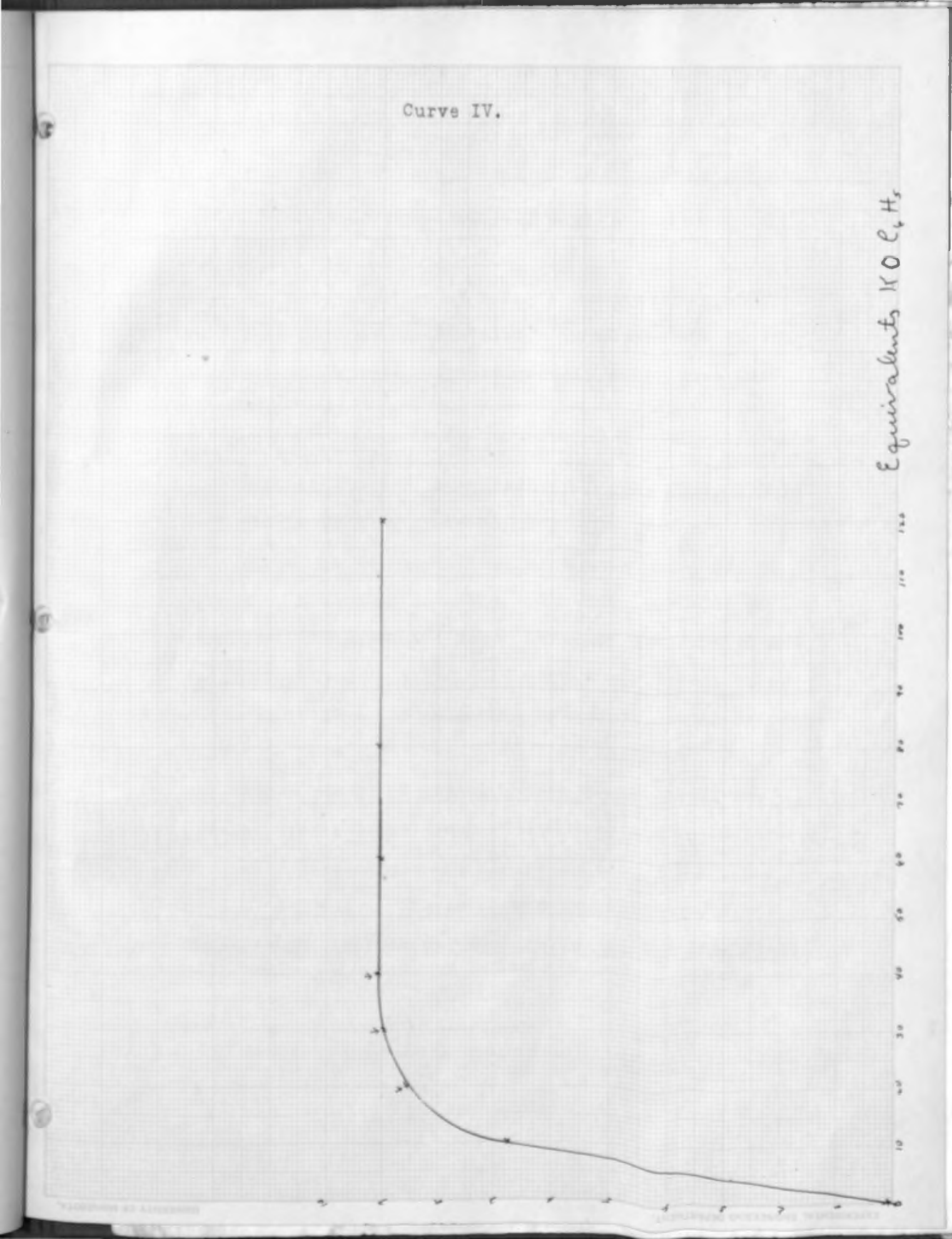
H O K

Curve III.

Recalculated from
Curve II.
C_2H_5OK constant,
K O H varying.



Curve IV.



Experimental Part.

A.— The determination of halogen removed from chloroform with constant concentration potassium and varying phenoxyl and hydroxyl simultaneously which gave Curve I.

Materials used:

15 c.c. $CHCl_3$

25 c.c. K O H 12.88 N, 48% by weight, spg. 1.507 at 15.6 0 g. to 30.29 g. C_6H_5OH.

Different determinations were made using 0%, 5%, 10%, 15%, 17%, 20%, 25%, 40%, 60%, 80%, and 100% of phenol. The grams of phenol for each determination were calculated by taking the amount equivalent to react with 18.07 g. of potassium hydroxide, which was contained in 25 c.c. of the 12.88 N solution as 100%. This was 30.29 g. of phenol. For 0% no phenol was present, for 10% one tenth of 30.29 g. and so on for the other percentages and always 25 c.c. K O H and 15 c.c. $CHCl_3$. The potassium hydroxide and phenol were brought to boiling under reflux by the free flame

in an Erlenmeyer flask protected from direct heat by a piece of asbestos. The flame was just sufficient to keep the mixture bubbling. As soon as the mixture began to boil the chloroform was added thru the condenser; the time at which the chloroform reached the mixture was noted to seconds, at the end of ten minutes the flame was extinguished and 25 c.c. of cold water were added thru the reflux. The contents of the flask were poured into 200 c.c. of cold water containing 20 c.c. of concentrated nitric acid. If the mixture was not acid more nitric was added until it was acidified. The chloroform, some of which was always left after each determination, was separated with a separatory funnel, washed twice with 50 to 60 c.c. of water which was added to the main volume. This was made up to 500 c.c. in a calibrated flask; 50 c.c. portions were removed with a calibrated pipette and titrated for ionized chlorine with silver nitrate and potassium sulphocyanate using a solution of iron alum acid with nitric, as an indicator. Calibrated burettes were used.

Perhaps the greatest error in the results obtained by the above method is the difference in temperature of the series. In preliminary determinations it was found that the temperature was very constant for a single per cent, but for the series it varied from 58° to 65°. The low temperatures correspond to the maximum amounts of chlorine removed. It was found that it would be very difficult to regulate the temperature, so it was decided to let this be one of the uncorrected errors. The boiling chloroform thoroughly stirred the mixture in this and the following determinations in which it was used, thus eliminating a large error for intimate contact was desired.

The color of the reaction mixture varied throughout from light yellow to a dark yellow. When chloroform was added to the phenolate mixture about the maximum a flocculent precipitate formed which dissolved when more chloroform was added.

The 20% determination was checked gravimetrically and a 50% determination also fell on the curve. In

these two the egg shaped flask and water bath were used heating until the phenol had dissolved and then the chloroform added. The rest of the technique was the same as above except that the chlorine was precipitated as silver chloride and weighed in a gooch.

Results:-

Percentage of Phenol	Grams of Phenol	"Choloroform" left after the reaction in c.c.*	Grams Chlorine removed in ten minutes
0	0	7.7 c.c. 9.0 c.c.	.281 .311
5	1.51	9.0	2.284
10	3.03	2.0	8.286
15	4.54	3.5	8.718
17	5.15	4.0	8.918
20	6.06	6.05	8.670
25	7.57	4.5	7.962
40	12.12	9.5	7.070
60	18.17	14.0	4.908
80	24.22	19.5	2.568
100	30.28	26.0 24.5	1.471 1.081 1.09

* In the higher per cents where apparently more chloroform was recovered than was added in the beginning, it was thought that it had dissolved some phenol.

The above data was plotted. The grams of chlorine are represented on the ordinate and the per cents of phenol on the abscissa. This gave a very smooth curve I to which correction curves I and II (mentioned later) were applied. From the same data curves II and III were plotted.

It is evident in the Reimer Tiemann reaction that some of the halogen is removed by the action of the potassium phenolate and some by the action of the potassium hydroxide. Therefore two correction curves were made in order to remove these errors.

Correction Curve I.

Halogen removed by varying concentration of potassium phenolate.

This was carried out in an egg-shaped flask, fitted with a reflux condenser by a ground glass joint. 25 c.c. of potassium hydroxide 13.90 N, 1.499 spg. at 20°, 48.29% by weight were taken as 100% and the equivalent amount of phenol as 100% phenol. Various determinations were made using different per cents of the hundred per

cent amounts always with 15 c.c. of chloroform for each. The potassium hydroxide was calculated on the per cent by weight so that the ten per cent contained 25 c.c. of the 4.8% potassium hydroxide by weight, also 10% of the 100% phenol. In correction curve II the calculation for hydroxide was the same and 25 c.c. of the desired per cent by weight were always used in a determination as in this curve, but no phenol was present. The method for this curve did not vary from that of the preceding experiment except that the heating was done on a boiling water bath and in each case the phenol and hydroxide were mixed heated until the phenol had all dissolved, the chloroform added and heated twenty minutes from that time.

The determinations for both correction curves were heated twenty minutes. One half of the amount of halogen removed in that time was used to correct Curve I. It was necessary to heat these twenty minutes as the amount of chlorine removed is so small that it would not be practical to deal with smaller amounts than obtained in that time.

In these determinations the color of the reaction mixtures was bright scarlet when the chloroform was first added but yellow on longer heating.

Results:-

Per cent of Potassium Phenolate	Grams Chlorine removed in twenty minutes
20	.0084
40	.0389
60	.0980
80	.2910
90	.6540
100	1.471 1.081 1.090

Since the normality of the potassium hydroxide was so nearly the same as that used for the preceding curve, it was decided to use the results obtained for the 100% of that curve for this one also.

Correction Curve II.

Halogen removed from Chloroform by potassium hydroxide alone.

The technique employed in the varying per cents

for this curve was the same as that for the first curve mentioned. The heating was done with the free flame and an Erlenmeyer flask used. The potassium hydroxide was 12.88 N and 48% by weight. The results obtained do not give a very regular curve, but as it is only a correction curve and the amounts of halogen are so small in comparison with the amounts in the large curve, it has been used. The 100% determination contained 25 c.c. of 12.88 N potassium hydroxide and 15 c.c. chloroform, while the 0% contained 25 c.c. water and 15 c.c. of chloroform.

Results:—

Per cent of potassium hydroxide	Grams of Chlorine removed in twenty minutes.
0	0.0000
4	0.3141
10	0.9490
20	1.0827
30	1.1995
45	1.0740
50	0.4560
70	0.4874
90	0.4940
100	0.3958, 0.3733

It was realized that further work should be done as other discordant results were obtained. Therefore

a curve was obtained by keeping the reaction mixture in the egg-shaped flask at a constant temperature of 55° for twenty minutes in a thermostat. The chloroform and potassium hydroxide were allowed to take the temperature of the bath before mixing. 50 c.c. of chloroform were used as the mixture was stirred by air. If a smaller amount was used none was left at the end of the reaction.

Results:—

Per cent of Potassium Hydroxide	Grams of Chlorine removed in twenty minutes.
0	0.0000
20	0.1680
35	0.3590
50	0.4955
75	0.2394
100	0.1316

Curve I should be repeated under the above conditions, but lack of time prevented it just now.

B.— Experiments on other Reactions of the same Type.

I. Those in which phenol and potassium hydroxide or potassium phenolate are used.

(a) Carbon Tetrachloride, Potassium Hydroxide and Phenol.

Determinations were made in an egg-shaped flask on a water bath according to the same technique and using the same proportions of phenol and potassium hydroxide with 15 c.c. of carbon tetrachloride, instead of chloroform, as in Curve I. It was found that the chloride was about one-sixteenth as reactive as the chloroform.

(b) Benzotrichloride, Phenol, and Potassium Hydroxide.

Materials

25 c.c. K O H (12.86 N)

6.06 g. C_6H_5OH *

15 c.c. $C_6H_5CCl_3$ { Washed with K O H, then water, dried with $CaCl_2$, re-distilled.

The phenol and potassium hydroxide were heated with a free flame in the egg until the potassium hydroxide had

* 6.06 g. C_6H_5OH corresponds to the 20% of the C_6H_5OH, K O H, C H Cl_3 reaction.

dissolved the phenol, then the benzotrichloride was added through the condenser. The reaction was slow at first then very violent; it was stopped in three or four minutes. At first the reaction mixture was a bright yellow, then a dark reddish yellow with a greenish tinge. The reaction mixture was poured into water, filtered, and a greenish, scaly precipitate was obtained on drying which was organic. The filtrate (A) was acidified with dilute hydrochloric; a precipitate formed which was filtered off. It was bright red and resinous. This was dissolved in 4% potassium hydroxide and carbon dioxide passed into the solution; a precipitate formed which at first was flocculent and afterwards resinous much like the former resinous precipitate. It was filtered (B). The filtrate (A) was evaporated by heat, reddish white crystals formed, probably benzoic acid, discolored by a slight amount of the red dye. These were taken up with water and filtered, some red crystals were left. The filtrate from B was extracted with ether, dried quickly with calcium chloride and

the ether, yellow in color, evaporated on a hot plate; a yellow oil was left. A red dye, probably benzaurin, was left in the alkaline solution which was partially evaporated and a white salt precipitated. The resinous mass obtained after passing carbon dioxide into the alkaline solution was dissolved in benzene; a flocculent precipitate formed, was filtered off, washed with benzene and dried. A red dye was left.

(c) Chloroformic Ester, Potassium Hydroxide and Phenol.

Materials

25 c.c. — K O H

6.06 g. C_6H_5OH

15 c.c. Cl C Ø Ø C_6H_5

The potassium hydroxide and phenol were heated in the egg with a free flame until the phenol had dissolved then the ester was added through the condenser. The reaction was rapid, a white crystalline solid separated out and there were two liquid layers. The heating was stopped in five minutes, the mixture taken

up with water, which dissolved the solid. The oil was separated, washed once with water and added to the water portion. The water portion was shaken twice with ether and the extracts added to the oil. The water portion was acidified with nitric acid, apparently no action. It was made just alkaline with potassium hydroxide and shaken twice with ether to remove the phenol. The ether extracts containing the oil were distilled and 6.86 g. of oil, probably ethylphenyl carbonate, obtained. After the water portion had been freed from phenol it was evaporated to dryness. All of the solid dissolved in water, the solution was faintly alkaline, it was acidified with dilute nitric, no precipitate was obtained (no salicylic acid). It was extracted once with ether and the ether allowed to evaporate. This did not contain salicylic acid.

(d) The Preparation of Potassium Phenolate.

Potassium phenolate was prepared by heating ten per cent excess of phenol with potassium hydroxide, which was dissolved in as little water as possible, in

an Erlenmeyer fitted with an air condenser until the excess of phenol had distilled over. The reaction mixture which solidified on cooling was re-crystallized from acetone (2-3 parts) and absolute alcohol (1 part). It was necessary to use a hot water funnel and suction to facilitate filtration. The phenolate was dried in a vacuum desiccator heated by steam until a constant weight was obtained.

(e) Trichloracetic Ester and Potassium Phenolate.

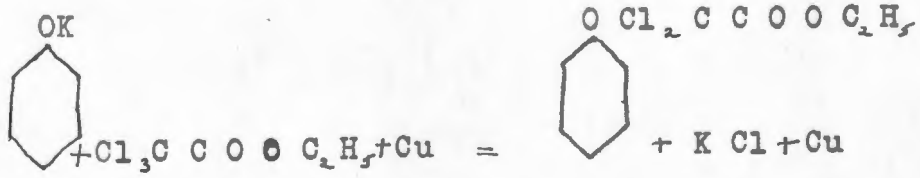
A reaction was obtained when a definite amount of dry potassium phenolate was treated with 10% excess of the ester, heat being evolved, the ester dissolving the salt and then the whole solidifying. This was treated with water, filtered, and tested for ionized chlorine which was not present.

Another determination was made in which the solidified mass was heated on a water bath for an hour but still no chlorine was obtained.

Both were repeated a little copper bronze being added in each case but no ionized chlorine was isolated.

In another experiment carried farther with these same compounds, the potassium phenolate used was not so dry or pure as that in the above experiments. This may account for the dense white fumes mentioned.

It was hoped that the reaction took place as here shown, but as no ionized chlorine could be found, no further work was done at that time.



Materials

C_4H_5OK — 69 g.

$Cl_3CCOOC_2H_5$ — 110 g.

Cu enough to slightly color the mixture.

The phenolate was finely pulverized, some copper bronze added and then the ester. At first there was no reaction, but on standing a few minutes the reaction began and dense white fumes were given off. The containing flask was fitted with a reflux condenser, after the fuming had ceased, and the reaction mixture was heated

slowly for an hour to an hour and one half. On heating the reaction mixture became almost black in color. When the heating was completed the mixture was cooled, treated with 200 - 300 c.c. of water to remove excess phenolate and potassium chloride, removed from the water by a separatory funnel, dried with calcium chloride and then fractionated.

This mixture after freed from calcium chloride was found to contain a crystalline solid which had precipitated. It was treated as follows: First with benzene and then sucked dry. This divided it into two parts, a benzene soluble part and a benzene insoluble part. The benzene soluble part contained some of the liquid which was poured off for fractionation. This liquid residue contained something precipitated by benzene. The benzene insoluble part contained something precipitated by benzene and also the crystals. This insoluble part was divided into two parts by alcohol. A soluble part, a reddish brown liquid which was allowed to evaporate. An insoluble part which was crystalline and almost white, probably calcium chloride

and potassium chloride, nearly all soluble in water. A small amount was dissolved in water and acid added, no precipitate was obtained. When a small piece was heated on platinum foil a large amount of ash was left. When the alcohol soluble part had evaporated to dryness, it was assumed upon testing to be calcium chloride crystallized with alcohol. The crystals were large and white. The soluble benzene part was also allowed to evaporate; it was a dark reddish brown color and exceedingly viscous. Before evaporating about 10 c.c. of this mixture which separated out as a lower layer was discarded, as it was thought to be water. It was a very light yellow color.

When the liquid spoken of in the beginning was fractionated the following fractions were obtained:

I	II	III	IV	V	VI
94°-96°	96°-100°	100°-120°	150°-185°	185°-220°	220°-240°
Fractionating column and small Erlenmeyer Oil bath condenser			Distilling flask only Air condenser and free flame		
Temperatures of bath-					
138°	140°-150°	150°-170°	170°-250°		

A black charred residue was left in the distilling flask. It was porous and smelled like burnt sugar, and salicylaldehyde.

Fractions I, II, III were each composed of two colorless immiscible liquids.

The top layers of I, II, III were then mixed and fractionated.

A		B	
92°-96° two layers		96°-108°	oil bath and water condenser temperature of bath 230°, fractionating column used.
(86°-90°) A_1	(90°-96°) A_2	(96°-108°) B	

Fractions obtained by combining lower layers of I, II, III and fractionating:

(70°-90°) (90°-110°) (110°-164°) (164°-167°)

(f) Pyridine, Potassium Phenolate, and Chloroform.

Materials:—

C_6H_5OK 8.48 g. (corresponds to 6.06 g. C_6H_5OH or 20% of Curve I)

$CHCl_3$ 15 c.c.

C_5H_5N 30 c.c.

The potassium phenolate was placed in an Erlenmeyer flask fitted with a reflux condenser, the pyridine was added, and the mixture heated until the phenolate had dissolved. A dark red colored solution was formed. When chloroform was added to this a precipitate separated and the color changed to dark brown. The mixture was heated five hours and fifty minutes, then treated as follows: Water was added until the chloroform separated out. The two liquids were separated after making acid with hydrochloric and filtered through dry funnels. One portion, a dark brown viscous liquid from which crystals separated on standing, did not give an aldehyde test with the fuchsin reagent.* The orange yellow water solution was extracted three times with benzene. An emulsion formed during each extraction. The light yellow benzene extract was shaken out with hydrochloric acid to remove pyridine present, dried with calcium chloride and benzene distilled off. About one cubic centimeter of a dark brown liquid was left which

* Fuchsin reagent used whenever aldehyde tests were made.

gave an aldehyde test. On standing crystals separated. Some of this liquid was treated with sodium bisulphite in which it dissolved.

II. Those in which phenol is used.

(a) Pyridine, Phenol, and Chloroform.

Materials:—

C_5H_5N 30.5 c.c.

C_6H_5OH 6.04 g.

C H Cl_3 15 c.c.

This was carried out as the preceding experiment. After heating when the water had been added to the mixture acid with hydrochloric a brown mobile liquid was obtained which gave an aldehyde test and a light yellow water solution. It was twice extracted with benzene. The colorless extracts were shaken with hydrochloric acid, dried with calcium chloride, and the benzene evaporated on the hot plate. A light brown liquid was obtained from which crystals formed. It gave no aldehyde test.

(b) Diphenylether, Potassium Hydroxide, and Chloroform.

Materials:—

$C_6H_5OC_6H_5$ 7.80 g.

K O H 25 c.c.

C H Cl_3 15 c.c.

C_2H_5OH a few c.c.

This was prepared as the two preceding but was not acidified before taking up with water. The mixture was taken up with water; the large amount of crystalline salt which formed was dissolved; chloroform and the ether were thrown out, which were separated from the light yellow water solution. The mixture of ether and chloroform was neutral. It gave an aldehyde test. The water solution was extracted with benzene. The colorless extracts were evaporated on the hot plate and a drop of a bright yellow oil was obtained which gave an aldehyde test.

(c) Calcium carbonate, Phenol, and Chloroform.

Materials:—

$CaCO_3$ 30 g.

C_6H_5OH 6.06 g.

$CHCl_3$ 15 c.c.

C_2H_5OH 50 c.c.

H_2O — 50 c.c.

The materials were mixed in an Erlenmeyer, fitted with a reflux. The mixture was stirred with air and heated four hours. The calcium carbonate was filtered off and the filtrate divided into two parts. One portion was made acid with sulphuric, extracted with ether, the ether evaporated on a hot plate, and the residue tested for aldehyde. Test negative. The second portion was made acid with nitric acid and tested for chlorine. A slight test was obtained. This was carried out hoping to prove that the function of the potassium hydroxide in the Reimer Tiemann reaction is to take care of the hydrochloric acid split out, and therefore that another inorganic base would act in the same manner.

III. Those in which methane halogen derivatives and potassium hydroxide are used.

(a) Carbon Tetrachloride and its action on Potassium Hydroxide.

Determinations were made on the water bath using the egg-shaped flask* and reflux in which 15 c.c. carbon tetrachloride were substituted for chloroform and 25 c.c. of potassium hydroxide° were used. The technique was the same as that for Correction Curve II. The chloride is much less reactive than the chloroform. The amounts of chlorine removed are so small that it is not practical, but using the same proportions as in the curve resulting from the action of potassium hydroxide and chloroform, the following interesting results were obtained:

Results:—

Per cent of K O H	Grams chlorine removed in twenty minutes
0	0.0000
10	0.0065 -.0046
15	0.0090 -.0097
30	0.0038 -.0058
40	0.0043 -.0047
50	0.0036 -.0041
60	0.0027 -.0029
100	0.0043 -.0054

* Used on water bath in III, a, b, c.

° K O H in III a, b, c, made up according to % by weight.

The great difference in duplicates is due to the fact that such a small amount of silver nitrate was used for titrations, that small differences caused a great error.

(b) Methylene Chloride and Potassium Hydroxide.

A few determinations were made using 15 c.c. methylene chloride instead of chloroform and 25 c.c. potassium hydroxide in the same proportions and according to the same method as Correction Curve II. It was found that its reactivity was comparable to carbon tetrachloride.

(c) Benzotrichloride and Potassium Hydroxide.

Determinations using 15 c.c. of benzotrichloride instead of chloroform with 25 c.c. of potassium hydroxide in the same proportions and according to the same method as Correction Curve II showed that a very small amount of chlorine was removed as in the case of carbon tetrachloride and methylene chloride.

Appendix.

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Curve III.

Value Calculated from Curve II.

Showing interpolated and extrapolated values for halogen removed, with C_6H_5OK constant and varying K O H.

Constant amount phenolate = 8.52 ≏ "30%"

Equivalents K O H. Added.	Halogen removed.
0% K O H	.08
1	2.21
2	4.53
3	6.28
4	8.57 (On Curve II)
5	10.
6.	12.09

Curve IV.

Value Calculated from Curve II.

Showing interpolated and extrapolated values for halogen removed, with K O H constant and varying C_6H_5OK.

Constant amount K O H = 14.46 g. $\simeq$ "80%"

Equivalents of Phenolate added.	Grams Halogen Calculated as Removed.
0	.08
1/8	6.75
1/4	8.57 (On Curve II)
3/8	8.98
1/2	9.08
3/4	9.00
1	9.04
1-1/2	9.00